An unusual alternating ferro- and antiferromagnetic 1D hydrogen-bonded μ_2-1,3-azide-bridged copper(II) complex: a dominant ferromagnetic coupling†

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A single-crystal structure analysis of $[Cu_2(bben)_2(N_3)_4]_n$ (**1**) [bben = 1,2-bis(benzylamino)ethane] revealed that the complex consists of double asymmetric μ_2-1,3-azide-bridged dimeric copper(II) moieties; each copper(II) coordinates with one bben, one terminal azido, and the two bridging azido ligands. The Cu–N_3–Cu torsion angle has a very large value of 47.5°. The dimeric units are assembled into 1D chains through N(bben)–H···N (azido) hydrogen bonds. The intra- and the interdimeric Cu···Cu distances in the chain are 5.281(2) and 3.662(2) Å, respectively. Magnetic measurements on **1** have revealed the existence of a dominant ferromagnetic interaction with exchange coupling parameters of $J_F = 16.8\ cm^{-1}$, and $J_{AF} = -3.6\ cm^{-1}$, using an alternating ferro- and antiferromagnetic chain model for $S = 1/2$ local spins. The ferro- and antiferromagnetic interactions are ascribed to the μ_2-1,3-azide bridges and the hydrogen bonds, respectively; the former interactions are rationalized by the large Cu–N_3–Cu torsion angles.

Azide-containing copper(II) complexes have received considerable attention due to their diverse structural and magnetic properties.[1] There are two main coordination modes for bridging azido ligands: end-to-end (EE) and end-on (EO). The end-on mode favors ferromagnetic interactions,[2,3] while the end-to-end mode generally mediates antiferromagnetic interactions.[4,5] Examples of complexes with ferromagnetic couplings mediated by EE azido ligands are very rare,[6–8] although such interactions are favored for complexes with very large M–$\mu_{1,3}$-N_3–M bond and torsion angles, according to theoretical calculations.[9] In this work, a one-dimensional complex $[Cu_2(bben)_2(N_3)_4]_n$ (**1**) [bben = 1,2-bis(benzylamino)ethane] has been synthesized, and it shows the unusual magnetic behavior of alternating ferro- and antiferromagnetic interactions, propagated by the asymmetric EE bridging azido ligands and hydrogen bonds, respectively.

Experimental

Materials and methods

All the reagents were used as received from commercial suppliers without further purification. ^{1}H NMR spectra were recorded on a Bruker AM-200 spectrometer. IR spectra were recorded on a Bruker Vector-22 spectrometer (KBr disk). Electronic reflectance spectra were obtained on a Shimadzu UV-3100 UV-Vis-NIR recording spectrophotometer. Microanalyses for C, H and N were carried out with a GmbH VarioEL elemental analyzer. EPR studies were performed with a Bruker ER200D-SRC spectrometer at the X-band (9.46 GHz). Magnetic susceptibility measurements of a polycrystalline sample of **1** were carried out on a Quantum Design MPMS7 SQUID magnetometer in a magnetic field of 1.0 T. Diamagnetism corrections were made using Pascal's constants;[10] a value of $60 \times 10^{-6}\ cm^3\ mol^{-1}$ was used for the temperature independent paramagnetism (TIP) of the Cu(II) ion.

Synthesis

The ligand bben·2HCl·MeOH was synthesized by a method similar to that reported by Sclafani *et al.*[11] Anal. found: C, 59.04; H, 7.66; N, 8.07; calc. for $C_{17}H_{26}Cl_2N_2O$: C, 59.13; H, 7.59; N, 8.11%. IR (KBr)/cm^{-1}: 3439 br, 2752, 2695, 1028, 742, 697. ^{1}H NMR (D_2O) δ: 7.45–7.51 (m, 10H, Ar–H), 4.29 (s, 4H, Ar–CH_2), 3.45 (s, 4H, CH_2CH_2).

A solution of bben·2HCl·MeOH (0.276 g, 0.80 mmol) neutralized with aqueous NaOH (1.6 mmol, 0.40 mL) in methanol (40 mL) was added dropwise to a stirred methanolic solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.296 g, 0.80 mmol). NaN_3 (0.104 g, 1.6 mmol), dissolved in a small volume of water, was then added slowly. The clear dark green solution was refluxed for 2 h, filtered to remove a small quantity of precipitate and left undisturbed at room temperature. After several days, the X-ray quality green single crystals that deposited were filtered off, washed with cold water, and air dried. Yield: 0.196 g, 63.1%. The analysis for the bulk material was consistent with the formula proposed. Anal. found: C, 49.82; H, 5.42; N, 28.84; calc. for $C_{16}H_{20}CuN_8$: C, 49.54; H, 5.20; N, 28.89%. IR (KBr)/cm^{-1}: 3238w, 3167w, 2947w, 2072s, 2032s, 1495w, 1454m, 1337m, 1207w, 1080w, 1059w, 1009m, 952w, 852w, 752m, 742m, 697s, 623m.

Crystal data collection and refinement

A single crystal was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV image plate area

† Electronic supplementary information (ESI) available: EPR spectra of **1** (Fig. S1) and fit of $\chi_M T$ data with the binuclear model (Fig. S2). See http://www.rsc.org/suppdata/nj/b1/b108511p/

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Table 1 Crystal data and details of the structure determination for **1**

Formula	$C_{32}H_{40}Cu_2N_{16}$
FW	775.86
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a/Å	8.1175(16)
b/Å	9.4246(19)
c/Å	12.362(3)
α/°	93.23(3)
β/°	109.13(3)
γ/°	97.09(3)
U/Å^3	881.9(3)
T/K	293(2)
μ(Mo-Kα)/mm^{-1}	1.263
R^a $[F > 2\sigma(F)]$	0.0557
$R_w{}^a[F > 2\sigma(F)]$	0.1252
No. meas. reflect.	3169
No. indep. reflect. (R_{int})	3169(0.0000)

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [[\sum\omega(|F_o| - |F_c|)^2]/\sum\omega F^2{}_o]^{1/2}$.

Table 2 Selected bond lengths (Å) and bond angles (°) for **1**

Cu(1)–N(3)	1.967(4)	Cu(1)–N(2)	2.032(4)
Cu(1)–N(1)	2.043(4)	Cu(1)–N(6)	2.044(4)
Cu(1)–N(8)#1	2.373(4)		
N(3)–Cu(1)–N(2)	160.37(17)	N(3)–Cu(1)–N(1)	90.12(18)
N(2)–Cu(1)–N(1)	84.34(16)	N(3)–Cu(1)–N(6)	94.37(18)
N(2)–Cu(1)–N(6)	89.02(17)	N(1)–Cu(1)–N(6)	171.40(15)
N(3)–Cu(1)–N(8)#1	100.34(18)	N(2)–Cu(1)–N(8)#1	98.68(17)
N(1)–Cu(1)–N(8)#1	92.14(16)	N(6)–Cu(1)–N(8)#1	94.27(16)
N(4)–N(3)–Cu(1)	126.0(4)	N(5)–N(4)–N(3)	176.4(6)
N(7)–N(6)–Cu(1)	113.5(3)	N(8)–N(7)–N(6)	176.2(5)
N(7)–N(8)–Cu(1)#1	142.6(4)		

detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of 20 ± 1 °C and corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections $[I > 2.00\sigma(I)]$ and variable parameters. All calculations were performed using the SHELX-97 software package.[12] Abbreviated crystal data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC reference number 173463. See http://www.rsc.org/suppdata/nj/b1/b108511p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Structure description

The single-crystal structure revealed that **1** consists of double asymmetric EE azido-bridged dimeric copper(II) moieties (Fig. 1). The copper(II) environment is distorted square pyramidal with a Reedijk[13] distortion index τ of 0.18 ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid). The basal plane is formed by four nitrogen atoms, two from bben, one from a terminal azide, and another one from a bridging azide group. The axial position is occupied by another bridging azide group. The Cu–N(bben) bond lengths [2.032(4) and 2.043(4) Å] are within the normal range.[14] The Cu–N (terminal azide) distance [1.967(4) Å] is the shortest, and the axial Cu–N bond is the longest [2.373(4) Å] in the coordination polyhedron. The

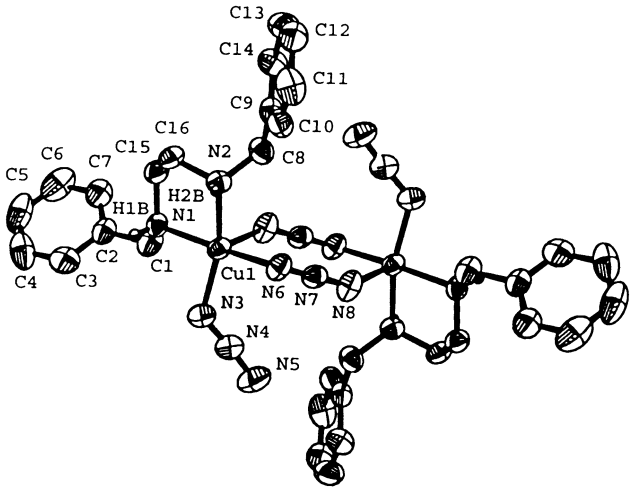

Fig. 1 The dicopper(II) unit of $[Cu_2(bben)_2(N_3)_4]_n$, showing the numbering scheme with the H atoms omitted for clarity.

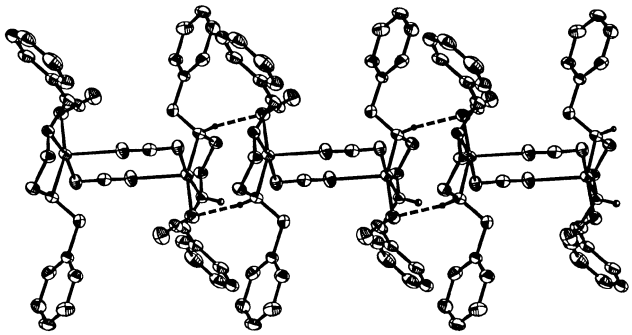

Fig. 2 Linear structure of $[Cu_2(bben)_2(N_3)_4]_n$ along the a direction, showing the hydrogen bonds between the dicopper(II) units.

Cu–azido angles are 113.5° for Cu(1)–N(6)–N(7) and 142.6° for Cu(1)–N(8)#1–N(7)#1.

The dimers are connected by hydrogen bonds between the coordinated amino groups of one dimer and the terminal azido nitrogen atoms of a neighboring dimer [N···N: 3.067(6) Å; N–H···N: 167.7°], giving a 1D chain (Fig. 2). The intra- and the interdimeric Cu···Cu distances are 5.281(2) and 3.662(2) Å, respectively.

IR, EPR and electronic spectra

The IR spectrum of **1** shows two sharp $\nu_{as}(N_3)$ stretching vibration bands at 2072 and 2032 cm^{-1}, consistent with the presence of EE and terminally bonded azides. The medium intensity band at 1337 cm^{-1} can be assigned to the $\nu_s(N_3)$ stretching mode.

Featureless EPR spectra were observed for polycrystalline samples of **1** at room temperature and at 100 K. In DMF solution, an isotropic spectrum containing four hyperfine lines is observed at room temperature, while the spectrum at 100 K has an axial symmetry, exhibiting four hyperfine peaks in the parallel region (see ESI Fig. S1) with $g_{\|} = 2.217$, $g_{\perp} = 2.013$ and $g_{iso} = 2.081$. The fact that $g_{\|} > g_{\perp}$ confirms a distorted square pyramidal stereochemistry with a $(d_{x^2-y^2})^1$ ground state in complex **1**.

The electronic reflectance spectrum of **1** shows a sharp band at 869 nm and a broad asymmetric band with a maximum at 697 nm, characteristic of a distorted square pyramidal CuN_5 coordination polyhedron.[15]

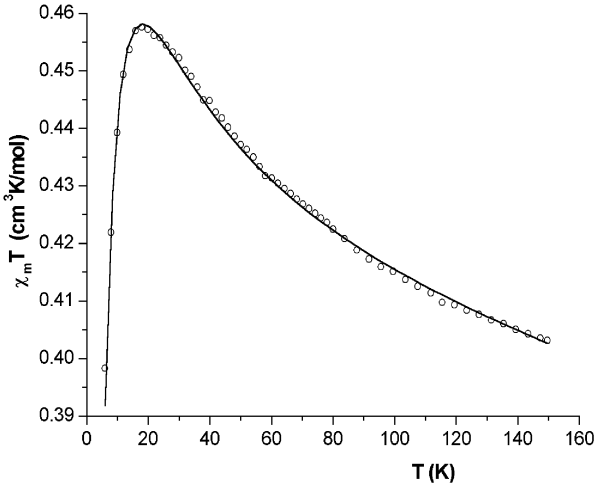

Fig. 3 Plot of the product $\chi_M T$ *vs.* temperature for **1**; the solid line represents the best fit of the data using the Georges equation (see text).

Magnetic properties

The product $\chi_M T$ for **1** (Fig. 3) gradually increases as the temperature is decreased, reaches a maximum of 0.4562 cm^3 K mol^{-1} at 20 K, and then decreases sharply at lower temperatures, which is indicative of a global ferromagnetic behavior for the compound. Since the shortest interchain Cu···Cu separation is 10.128(2) Å, appreciable interchain magnetic interactions can be ruled out. As hydrogen bonds have been reported to propagate antiferromagnetic interactions between metal centers in a variety of transition metal complexes,[16] the interdimeric interactions through the hydrogen bonds are expected to be weakly antiferromagnetic. EE azido bridges are well known to mediate antiferromagnetic interactions, however, ferromagnetic interactions are favored for complexes with very large M–$\mu_{1,3}$-N_3–M bond and torsion angles, according to theoretical calculations.[9] Considering the fact that the torsion angles are very large in complex **1**, the ferromagnetic interactions indicated by the magnetic data may be mediated by the EE azide ligands. Thus, we have fitted the data in the following two ways.

(a) Assuming the interdimeric coupling through the hydrogen bonds is zero, the susceptibility data are fitted as a ferromagnetically coupled dinuclear complex. When the whole curve was fitted in this way, no reasonable result was obtained. Then we tried to fit the data between 150 and 20 K, with the data below 20 K being neglected. In this case the best fit parameters are: $J = 15.4$ cm^{-1}, $g = 2.12$ and $R = 8.5 \times 10^{-4}$ (see ESI, Fig. S2).

(b) Taking into consideration possible antiferromagnetic interactions through the interdimeric hydrogen bonds, the system was treated as an alternating ferro- and antiferromagnetic chain. Consequently, the magnetic data for **1** was analyzed with the Hamiltonian $\boldsymbol{H} = -J\sum(\boldsymbol{S}_{2i}\boldsymbol{S}_{2i-1} - \alpha\boldsymbol{S}_{2i}\boldsymbol{S}_{2i+1})$, where J is the coupling parameter associated with a particular copper(II) pair and αJ is the exchange constant associated with the adjacent unit (α being defined as $J_F/|J_{AF}|$).

The equation for an alternating ferro- and antiferromagnetic Heisenberg chain, derived by Georges *et al.*,[17] was used to analyze the magnetic data. The least-squares fitting gives $J_{AF} = -3.6$ cm^{-1}, $J_F = 16.8$ cm^{-1}, $g = 2.10$, $\alpha = 4.63$ and $R = 2.4 \times 10^{-4}$ (Fig. 3).

The latter fit gives a better interpretation compared to that of the former because the R value is much smaller and the fit can satisfactorily describe all the experimental data, and the deduced g value is in satisfactory agreement with the experimental one. The results imply that the weak antiferromagnetic interactions through the interdimeric hydrogen bonds cannot be neglected and that rather unusually strong ferromagnetic couplings through the axial asymmetric EE bridging azides occur in **1**. To our knowledge, ferromagnetic interactions through single EE azido bridges have been observed for only three transition metal complexes, varying from very weak ($J < 1$ cm^{-1}) for the copper(II) complexes $[Cu_3(atrz)_2(N_3)_6]$ and [Cu(benzylamine)$(N_3)_2$] to moderate ($J = 6.91$ cm^{-1}) for the nickel(II) complex $[\{Ni(5\text{-methylpyrazole})_4(N_3)\}_n](ClO_4)_n$.[6–8] The ferromagnetic interactions through the double EE azido ligands in complex **1** are rather strong, compared with those reported in the literature. We attempted to explain this result in terms of the large Cu–N_3–Cu torsion angle of 47.5°, which may minimize the antiferromagnetic contribution and favor the ferromagnetic interaction.[9] Investigations on the magnetostructural correlation for various asymmetrical double EE azido-bridged pentacoordinate Cu(II) complexes suggested that the main factor governing the antiferromagnetic interactions through the EE azido ligands is the distortion index τ of the copper(II) center.[18] To further elucidate this relationship, especially on the ferromagnetic side, the J coupling constants for the asymmetrical end-to-end azido-bridged pentacoordinate Cu(II) complexes together with their structural parameters are summarized in Table 3. It can be seen that antiferromagnetic interactions through the double EE azide ligands are observed for the complexes with torsion angles (Δ) less than 30.5°, and ferromagnetic interactions are observed for the complexes with torsion angles greater than 32°. Thus, the rather strong ferromagnetic interactions through the double EE azido bridges in complex **1** may be attributed to the large torsion angle of 47.5°. Due to the lack of examples with ferromagnetic interactions through double EE azide ligands, no further magnetostructural correlations have been conducted. However, it can be concluded from the above discussions that, in addition to the distortion index τ, Δ is the dominant factor governing the magnetic coupling, probably the ferromagnetic contribution, through the end-to-end azido ligands.

Table 3 Selected magnetostructural data for asymmetrical end-to-end azido-bridged pentacoordinate copper(II) complexes

Complex[a]	R[b]/Å	τ	Δ[c]/°	J/cm^{-1}	Ref.
$[Cu_2(\mu\text{-}N_3)_2(Me_5dien)_2](ClO_4)_2$	2.33	0.23	15.7	−7.5(6)	18[d]
$[Cu_2(\mu\text{-}N_3)_2(EtMe_4dien)_2](ClO_4)_2$	2.28	0.28	30.4	−3.6(4)	18[d]
$[Cu(benzylamine)(N_3)_2]_n$	2.33	0.01	38.2	0.40	7[e]
$[Cu(atrz)_2(N_3)]NO_3$	2.53	0.10	32.3	0.86	6[e]
$[Cu_2(bben)_2(N_3)_4]_n$ (**1**)	2.37	0.18	47.5	16.8	This work[d]

[a] Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine, $EtMe_4dien$ = 4-ethyl-1,1,7,7-tetramethyldiethylenetriamine. [b] Axial azide nitrogen–copper bond length. [c] Cu–N_3–Cu torsion angle (not mentioned in the original articles, and calculated from the supplementary materials obtained from the CCDC). [d] Double bridge. [e] Single bridge.

Conclusion

An asymmetric double μ_2-1,3-azide-bridged copper(II) complex $[Cu_2(bben)_2(N_3)_4]_n$ (**1**) with a very large Cu–N_3–Cu torsion angle has been synthesized. The dimeric units are assembled into 1D chains through interdimeric hydrogen bonds. A behavior of alternating ferro- and antiferromagnetic interactions showing an overall intrachain ferromagnetic interaction has been observed for **1**. The ferromagnetic interactions through the EE azide bridges are ascribed to the large Cu–N_3–Cu torsion angle.

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